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ON SOME DERIVATIVES OF PHENYLETHERS
II. REPORT

C. Häussermann and E. Bauer

Translation of "Über einige Abkömmlinge des Phenyläthers," Berichte Deutsche Chemischen Gesellschaft, Vol. 29, 1896, pp. 2083-2085.

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16. Abstract

Products and their synthesis of chloronitrobenzol with certain phenolates are discussed, as is the *p*-oxyphenylether occasionally produced. Yield, melting point, and physical description are given for each product. The products include 2,4'-dinitrophenylether; 2,2'-dinitrophenylether; *p*-nitrophenylether-*p*-oxybenzoic acid and its methylester; *p*-aminophenylether-*p*-oxybenzoic acid, its sulfate, and its barium salt; and *p*-oxyphenylether.

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ON SOME DERIVATIVES OF PHENYLETHERS
II. REPORT

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The behavior of chloronitrobenzol with certain phenolates /2083* outlined in an earlier paper[1] has been studied by us in the meantime, and in what follows we shall describe the products obtained as well as the *p*-oxyphenylether occasionally produced.

2,4'-Dinitrophenylether

To produce this compound, the strongly colored reaction product formed at 140° between *p*-chloronitrobenzol and *o*-nitrophenol potassium is treated with steam, then vacuum distilled. The distillate is repeatedly crystallized in glacial acetic acid and then finally in alcohol.

Analysis: calculated for $C_{12}H_8N_2O_5$.
percentages: C 55.38, H 3.08, N 10.80.
found " " : " 55.39, " 3.20, " 11.05.

The 2,4'-dinitrophenylether forms long, white needles which melt at 103.5° and dissolve in approximately 210 times their weight of alcohol at 17.5° or in 5.5 times their weight of boiling alcohol.[2]

If the ether is treated in alcoholic solution with tin and hydrochloric acid, then it is transformed to a chlorohydrate (found: Cl 25.4% calculated for $(C_6H_4N\ H_2)_2O\ .\ 2\ HCl$: 26.0%)), from whose aqueous solution a base with a melting point of 78-80° can be

*Numbers in the margin indicate pagination in the foreign text.

[1]This publication, Vol. 29, p. 1446.

[2]We could not isolate this dinitrophenylether from the product produced by the action of concentrated nitric acid on phenylether; whereas it was easy to separate the previously described isomer with melting point 143.5°, in pure form.

precipitated with ammonia.

2,2'-Dinitrophenylether /2084

The preparation attained by analogous means from *o*-chloronitrobenzol and *o*-nitrophenol potassium forms dull, white needles, when crystallized from alcohol, that melt at 114.5°.

Analysis: found percentages: C 55.02, H 3.10, N 11.05.

One part of the substance requires approximately 150 parts alcohol at 20° or 3.8 parts boiling alcohol to dissolve it. Reduction in acid solution produces a diamine which we are still investigating.

p-Nitrophenylether-*p*-Oxybenzoic Acid

This compound is obtained by adding dipotassium-*p*-oxybenzoate[3] at 160°, with constant stirring, to a large quantity of *p*-chloronitrobenzol. The temperature is then gradually raised and finally kept at 235° for approximately 6 hours. The melt is then dissolved in dilute sodium hydroxide solution, the unreacted chloronitrobenzol is filtered off, and the filtrate is mixed with hydrocloric acid. The ether acid thus precipitated is siphoned off, washed, and after drying, recrystallized in simmering alcohol, after which it is obtained in the form of small colorless prisms.

Analysis: found for $C_{13}H_9N\,O_5$.
percentages: C 60.23, H 3.48, N 5.41.
found " " : " 60.40, " 3.71, " 5.7.

The *p*-nitrophenylether-*p*-oxybenzoic acid $\overset{4}{N}O_2C_6H_4OC_6H_4\overset{1}{C}OOH$, melts at 236-237°. It is insoluble in water and only slightly

[3]The dipotassium salt of *p*-oxybenzoic acid is produced by introducing a hot, absolute alcohol solution of 1 Mol of the acid in a similar 2 Mol solution potassium alcoholate, siphoning out the precipitated salt and drying it over a water bath.

soluble in hot alcohol, ether, and chloroform.

The barium salt obtained from the free acid and barium carbonate (calculated: Ba 20.98%; found: 20.79%) crystallizes from a hot aqueous solution in a nonhydrated state.

The methylester (calculated: N 5.2%; found: 5.2%) is obtained by treating the acid with alcohol and hydrogen chloride in a waterbath and precipitating the product by adding water, then recrystallizing the precipitate in alcohol. This process yields matted needles that melt at 108-109° and are easily soluble in benzol.

p-Aminophenylether-*p*-Oxybenzoic Acid

The nitro acid is warmed for some time in a water bath with tin and hydrochloric acid with the addition of some alcohol. The fluid is then diluted and freed of alcohol by heating, freed of tin with hydrogen sulfide, and finally concentrated by filtration and cooled to yield a poorly soluble chlorohydrate. Acetic acid /2085 precipitates the free amido acid from the alkali solution of the chlorohydrate, which, after recrystallization in alcohol, yields yellowish-white, atmospherically stable platelets.

Analysis: calculated for $C_{13}H_{11}NO_3$.
percentages: C 68.12, H 4.8, N 6.11.
found " " : " 67.91, " 5.0, " 6.50.

The *p*-aminophenylether-*p*-oxybenzoic acid $NH_2C_6H_4OC_6H_4COOH$ melts at 193-194°. It is only slightly soluble in water and more soluble in alcohol and chloroform. The chlorohydrate (Cl calculated for $(C_6H_4)_2O \cdot COOH \cdot NH_2 \cdot HCl$ 13.37%; found: 13.21%) forms weakly gray scales, slightly soluble in cold water.

The sulfate (H_2SO_4 calculated for $[(C_6H_4)_2O \cdot COOH \cdot NH_2]_2H_2SO_4$ 17.62%; found: 17.78%) consists of a crystalline powder which

dissolves only with difficulty in cold water.

The barium salt produced from the free acid and the barium carbonate (Ba calculated for $[(C_6H_4)_2O \cdot NH_2COO]_2Ba$ 23.1%; found: 22.9%) is easily soluble in warm water and crystallizes therefrom in the form of white needles, while the very easily soluble sodium salt forms silky crystals.

With the usual azo-compounds, such as resorcinol, salicylic acid, naphthol- and naphthylaminsulfonic acids, the acid yields, after diazotizing, yellow to red dyes which are taken up by wool in an acid bath.

p-Oxyphenylether

The conversion of the *p*-aminophenylether into the corresponding phenol is easily accomplished, even if not without some loss, by means of boiling with excess amounts of hydrochloric acid and the calculated amount of nitrite containing solution. The raw phenol which separates in the form of a black oil is purified by vacuum distillation and subsequent recrystallization from a mixture of equal volumes of benzol and petrolbenzin. Finally, the product is dissolved in hot water from which it precipitates after cooling in the form of very fine, white, matted needles.

Analysis: calculated for $C_{12}H_{10}O_2$.

percentages: C 77.42, H 5.38.

found " " : " 77.28, " 5.60.

The *p*-oxyphenylether melts at 84-85° and is easily soluble in the ordinary solvents with the exception of water in which it dissolves only with difficulty at room temperature. The cold aqueous solution is not colored by iron chloride.

With diazobenzolchloride, the alkaline solution yields a brown-red dye.

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